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Thermochemical Dissociation of Water and Carbon Dioxide via ZnSI Cycle for Hydrogen and Carbon Monoxide Production

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Abstract

Thermochemical water and carbon dioxide splitting via zinc sulfur iodine (ZnSI) cycle coupling with renewable energy sources as the source of high temperature process heat, is a promising solution to produce hydrogen and carbon monoxide, which can alleviate CO_2 emissions from the combustion of various fossil fuels. The synthetic liquid fuels are achieved with the combination of CO and H_2. The process design of this novel approach has been carried out on the basis of six associated chemical reactions. The theoretical maximum energy conversion efficiency of the cycle has been evaluated according to basic thermodynamic laws.

Keywords: thermochemical cycle; zinc sulfur iodine; carbon dioxide; hydrogen; thermal efficiency estimation

1. Introduction

The continuous rise in anthropogenic atmospheric CO_2 concentrations, and accelerated growth in the extensive use of fossil fuels, such as coal, oil, and natural gas result in the serious global greenhouse effect [1,2]. Therefore, the reduction of CO_2 emissions as a major global issue has attracted increasing attention in recent years. Carbon dioxide as a major greenhouse gas (GHG) significantly contributes to the present trend of global warming, causing environmentally harmful effect. Recycling CO_2 as carbon-source for

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chemical fuels using any alternative energy source, such as solar, geothermal, and even hopefully safe nuclear energy, is needed for the development of a large-scale cost-effective sustainable energy system.

The "thermochemical cycle" offers a method for transforming heat energy into carbon monoxide and hydrogen, the energy carriers. In contrast to direct thermal decomposition of CO_2 and H_2O at high temperatures, thermochemical approaches to CO_2 and H_2O decomposition operate at appropriate lower temperatures by combining high temperature endothermic chemical reactions and low temperature exothermic chemical reactions. As such, they provide an attractive route to fuel production at high rates and efficiencies without precious metal catalysts [3], which using redox chemical reactions further bypass the CO-H_2-O_2 separation problem [4]. Two step thermochemical cycles based on metal oxide redox pairs (mainly Zn/ZnO, Ce_2O_3/CeO_2, FeO/Fe_3O_4 and SnO/SnO_2) to date have largely been studied, which are driven by high temperature process heat, derived from concentrated solar energy [4-14]. The main challenges are the need of fast quenching of gaseous products to avoid their recombination [4] and a complete conversion of metal to metal oxide to implement promising fast carbon monoxide and hydrogen production rates [10]. Two step thermochemical metal/metal oxide cycles are described by the following chemical reactions.

$$M_xO_y \rightarrow M_xO_{y-1} + \tfrac{1}{2}O_2(g) \quad (1)$$

$$M_xO_{y-1} + CO_2(g) \rightarrow M_xO_y + CO(g) \quad (2)$$

$$M_xO_{y-1} + H_2O(g) \rightarrow M_xO_y + H_2(g) \quad (3)$$

The net effect of reactions (1)–(3) is the desired decomposition of water and carbon dioxide by the means of the metal oxide as a catalyst.

2. Conception of the ZnSI Cycle

Here we present a new thermochemical approach making use of Zn/ZnO/ZnI_2 recycling agents, which also involves in the sulfur iodine (SI or IS) thermochemical cycle. In this case an excess of iodine and water is used to induce sulfuric acid and hydrogen iodide separation [15]. The flowsheet designed for the purposes of demonstrating this novel cycle is schematically shown in Fig. 1. The proposed cycle is based on a series of six underlying reactions described by the reactions (4)–(9).

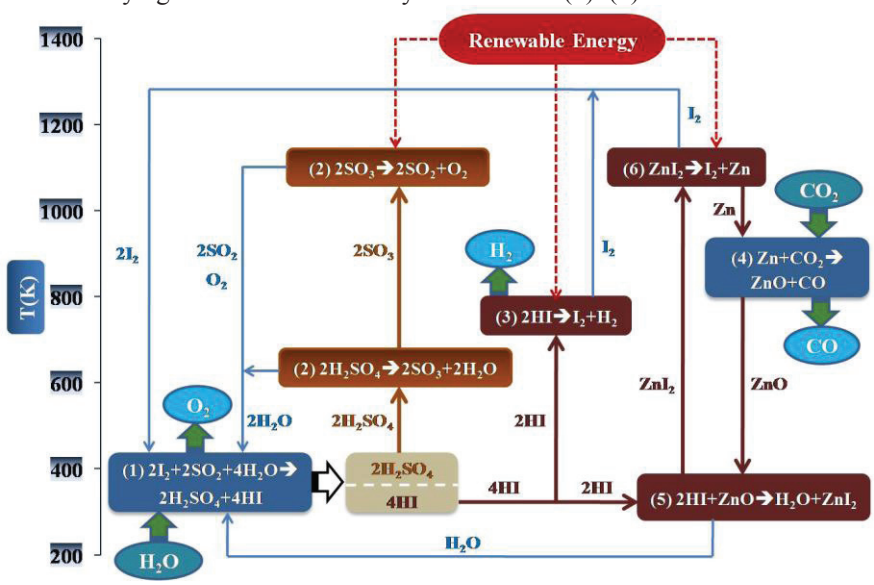

Fig. 1. Schematic of the novel thermochemical carbon dioxide and water splitting cycle

$$2I_2+2SO_2(g)+4H_2O \rightarrow 2H_2SO_4(aq)+4HI(aq) \quad (4)$$

$$2H_2SO_4 \rightarrow 2SO_2(g)+2H_2O+O_2(g) \quad (5)$$

$$2HI \rightarrow I_2+H_2(g) \quad (6)$$

$$Zn+CO_2(g) \rightarrow ZnO+CO(g) \quad (7)$$

$$2HI(aq)+ZnO \rightarrow ZnI_2+H_2O \quad (8)$$

$$ZnI_2 \rightarrow Zn+I_2 \quad (9)$$

The reactions (4)–(6) are the critical steps in the SI thermochemical water splitting cycle. Bunsen reaction (4), which is performed at 293–393 K with an excess of water and iodine, produces two non-miscible liquid phases: H_2SO_4 phase and HIx phase. According to the reactions (5) and (6), the separated H_2SO_4 and HIx phase solutions are decomposed to produce oxygen and hydrogen at 1073–1273 K and 573–773 K, respectively. In the reaction (7) (namely CO_2 reduction reaction), carbon monoxide and zinc oxide are produced via the exothermic oxidation of zinc by carbon dioxide. The generated zinc oxide spontaneously reacts with hydrogen iodide, which is derived from HIx phase solution, to produce zinc iodide aqueous solution in the reaction (8). The zinc iodide obtained is decomposed to regenerate the recycling agents zinc and iodine by the endothermic reaction (9). In such a way, the dissociation of carbon dioxide and water into carbon monoxide, hydrogen and oxygen is achieved with only the input of carbon dioxide, water and the proper high temperature process heat.

In this study, thermal efficiency evaluation of the ZnSI cycle was conducted to establish reaction and cyclic system feasibility.

3. Thermal Efficiency Estimation

The common definition of thermal efficiency in thermodynamics is given by the fraction of the heat input that is covered to net work output. For our ZnSI cycle, the net work output is the recoverable energy from the cycle, which equals to the enthalpy value of the formations of water and carbon dioxide. The heat input is the total heat requirement of the cycle. The thermal efficiency formula should be described as:

$$\eta_{th} = \frac{\left|\Delta H^0_{H_2O}(T_a)\right| + \left|\Delta H^0_{CO_2}(T_a)\right|}{Q + W/\eta_r} \quad (10)$$

Where Q and W are the heat and work requirements and η_r = 0.5 the conversion efficiency of the system. $\Delta H^0_{H_2O}(T_a)$ and $\Delta H^0_{CO_2}(T_a)$ are the enthalpies of the hydrogen and oxygen recombination reaction and carbon monoxide and oxygen recombination reaction at ambient temperature and pressure. The values are -286 and -283 kJ/mol, respectively. We use all of the assumptions that Goldstein and Wang et al. have used in the calculation of the heat Q and work W required by the cycle [16,17]. Assuming all reactions reversible, Q and W requirements of each reaction based on thermodynamic laws are listed as follows:

$$Q = T\Delta S = \Delta H - \Delta G \quad (11)$$

$$W = \Delta H - T\Delta S = \Delta G \quad (12)$$

If the reaction is exothermic, the heat requirement is lost. In addition, if the system produces work, there is no work needed. Consequently the total energy requirement for each reaction is shown as follows:

$$\Delta G/\eta_r + (\Delta H - \Delta G), \text{ if } \Delta H - \Delta G > 0 \quad (13)$$

$$\Delta G/\eta_r, \text{ if } \Delta H - \Delta G < 0 \quad (14)$$

Due to phase changes or separations represented by the independent reactions, the detailed process of the ZnSI cycle based on reactions (4)–(9) is described as the following equations, in which the physical states of the involved substances and reaction temperatures are specified.

$$32H_2O(l)+18I_2(l)+2SO_2(g) \rightarrow (2H_2SO_4+8H_2O)_{L1}+(4HI+20H_2O+16I_2)_{L2} \text{ (400 K)} \quad (15)$$

$$(2H_2SO_4+8H_2O)_{L1} \rightarrow 2H_2SO_4(l)+8H_2O(l) \text{ (570 K)} \quad (16)$$

$$2H_2SO_4(l) \rightarrow 2H_2SO_4(g) \text{ (630 K)} \quad (17)$$

$$2H_2SO_4(g) \rightarrow 2SO_3(g)+2H_2O(g) \text{ (670 K)} \quad (18)$$

$$2SO_3(g) \rightarrow 2SO_2(g)+O_2(g) \text{ (1140 K)} \quad (19)$$

$$Zn(l)+CO_2(g) \rightarrow ZnO(s)+CO(g) \text{ (1123 K)} \quad (20)$$

$$(4HI+20H_2O+16I_2)_{L2} \rightarrow 4HI(g)+(20H_2O+16I_2)_L \text{ (500 K)} \quad (21)$$

$$2HI(g) \rightarrow H_2(g)+I_2(l) \text{ (600 K)} \quad (22)$$

$$2HI(g)+ZnO(s) \rightarrow ZnI_2(aq)+H_2O(l) \text{ (353 K)} \quad (23)$$

$$ZnI_2(aq)+H_2O(l) \rightarrow ZnI_2(s)+H_2O(l) \text{ (400 K)} \quad (24)$$

$$ZnI_2(g) \rightarrow Zn(l)+I_2(g) \text{ (923 K)} \quad (25)$$

Only reactions (20) and (23)–(25) are new and have never been discussed in references 4 and 5. The thermodynamic data of these reactions were calculated using FastSage version 5.2. The pumping work for the process is needed when pressure increase occurs according to the assumption of Goldstein and Wang et al [16,17]. The calculation results for the upper bound of thermal efficiency of the ZnSI cycle are summarized in Table 1.

Table 1. Upper bound of thermal efficiency estimation of the ZnSI cycle

	Reaction number	$Q+W/\eta_r$ kJ
	15	0
	16	196
	17	116
	18	188.6
	19	204.2
	20	0
	21	398
	22	24
	23	0
	24	43.1
	25	103.5
Pumping W/η_r	34	
$\Sigma(Q+W/\eta_r)$	1307.4	
$\lvert\Delta H^0_{H_2O}(T_a)\rvert$	286	
$\lvert\Delta H^0_{CO_2}(T_a)\rvert$	283	
η_{th}	0.435	

According to these thermodynamic data, an upper bound of the thermal efficiency is 43.5 %. It is noticed that the separation steps (Eqs. (16) and (21)) and sulfuric acid decomposition steps (Eqs. (18) and (19)) are the most energy consuming processes.

4. Conclusions

Thermochemical splitting of water and carbon dioxide for hydrogen and carbon monoxide production has been proposed to meet the needs of renewable energy development and CO_2 emission reduction. The basic flowsheet was designed to proceed this novel technology, and an upper bound of the thermal efficiency of the cycle was calculated according to the basic thermodynamic laws. The maximum thermal efficiency of 43.5 % was achieved.

Acknowledgements

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